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Strategies and Techniques for Sample Collection and Analysis: Experience from the Swedish PCB Accidents

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A series of polychlorinated biphenyl (PCB) fires and explosions in PCB-filled capacitors and transformers is discussed. A sampling program followed by isomer specific determination of trace levels of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) is described. Data from a series of Swedish PCB accidents are given. In addition to PCDFs and PCDDs, we have also found a series of polychlorinated biphenylenes (PCBPs). Cleaning of contaminated areas was done by vacuum cleaning followed by high pressure washing.

Introduction

Polychlorinated biphenyls (PCBs) have been used extensively as a dielectric fluid in capacitors and transformers since the 1950s. However, the use pattern in different countries is different (Table 1). It was found that commercial PCB mixtures solidified around -20°C, consequently, in Scandinavia where most transformers are placed outdoors, mineral oil is the most commonly used dielectric fluid in transformers.

In 1978 it was reported by Buser, Bosshardt, and Rappe that polychlorinated dibenzofurans (PCDFs) were formed in 1 to 25% yield by the pyrolysis of PCBs in the presence of air (*1*). This paper also contains a warning for all accidental and planned burning of PCBs or PCB-contaminated wastes.

During the period 1981 to 1983 a series of accidents were reported in Scandinavia and the United States that can illustrate this risk. These accidents can be subdivided into three different categories: (a) PCB fires with mineral oil as the external energy source; (b) PCB fires with electrical energy as the external energy source; (c) explosions in PCB-filled capacitors.

Some of these accidents are listed in Table 2, and some of these fires are also discussed in this article. These accidents all resulted in the formation of PCDFs, and in some cases also polychlorinated dioxins (PCDDs), biphenylenes (PCBPs), and pyrenes (PCPYs). It is generally accepted that a risk evaluation should be based on levels of the toxic 2,3,7,8-substituted congeners (Cl_4-Cl_6) (Figs. 1–3). Consequently, a highly sensitive and an isomer-specific analytical method is required. In Sweden an inofficial guideline for levels of PCDFs after

Table 1. Production and use of PCBs.

			PCBs, tons
PCB	Total world production		6000,000
	In electrical equipment		450,000
	Still in use (total)		150,000
	In electrical equipment		90,000
Transformers	USA	40,000 units	34,000
	Sweden	200 units	200
Capacitors	USA	2,800,000 units	40,000
	Sweden	100,000 units	2,000

Table 2. PCB accidents during 1981–1983.

Location	Category[a]	Date
Binghamton, NY, USA	b	February 5, 1981
Stockholm, Sweden	c	August 25, 1981
Skövde, Sweden (Volvo)	a	March 19, 1982
Arvika, Sweden (Volvo)	c	May 1982
Imatra, Finland	c	August 2, 1982
Helsinki, Finland	c	August 1982
Surahammar, Sweden	a	September 23, 1982
Hallstahammar, Sweden	c	November 8, 1982
Railway locomotive, Sweden	c	Winter 1982/83
Kisa, Sweden	c	April 25, 1983
San Francisco, CA, USA	b	May 15, 1983
Halmstad, Sweden	c	August 15, 1983

[a]See text.

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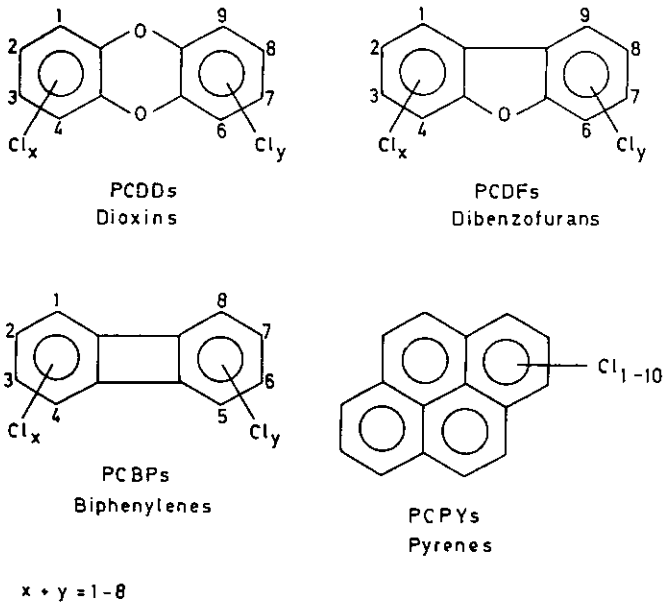

FIGURE 1. Structures of the compounds discussed.

PCB fires has been established: 2,3,7,8-tetra-CDF, 50 ng/m^2; total level of tetra-CDFs, 100 ng/m; total level of Cl_4-Cl_8 PCDFs, 1000 ng/m^2.

Experimental

Sampling, Extraction and Clean-up

A wipe test sample was collected by using a filter paper or Kleenex tissue. The sampled area was normally 2 dm^2. A dry wipe was followed by a wet wipe with water. An organic solvent was found to increase the background noise. The levels are given in amount per square meter (ng/m^2).

The sample (dried filter paper or Kleenex tissue from wipe tests or soot sample) was spiked with 1–2 ng of $^{13}C_{12}$-2,3,7,8-tetra-CDD, $^{13}C_{12}$-2,3,7,8-tetra-CDF and $^{13}C_{12}$-octa-CDD. Thereafter the sample was treated with 10 mL of 1 M hydrochloric acid for 1 hr with shaking. The slurry was filtered by suction on a Buchner funnel, washed with water, and dried in the air.

The dried material was transferred to a Soxhlet extractor and extracted with toluene (about 100 mL) for 8 to 48 hr at a speed of 1 to 2 mL/min. The toluene was evaporated to 100 μL in a Rotavapor with some external heating. The rest of the solvent was eliminated by a purified N_2 flush without external heating. The residues were dissolved in 1 mL of *n*-hexane and added to a silica gel column prepared from 0.5 g of Kiselgel 60, 70 to 230 mesh (Merck), stored in 130°C, and eluted with 5 mL of *n*-hexane. The hexane was evaporated to 100 μL by using a stream of nitrogen, and 2 μL of this solution was used for the analysis of PCPYs. The PCDDs and PCDFs were separated from other polychlorinated impurities by using an Alox-column (1.0 g basic alox activity 1, Woelm, ICN West Germany, stored at 190°C). The first fraction consisting of 1 mL *n*-hexane and 4 to 6 mL of *n*-hexane: methylene chloride (98:2) was discharged. The second fraction, 10 mL *n*-hexane: methylene chloride (1:1) was collected and evaporated until dryness in a stream of nitrogen. The residue, dissolved in a known amount of solvent (100 μL), was used for the GC/MS analyses.

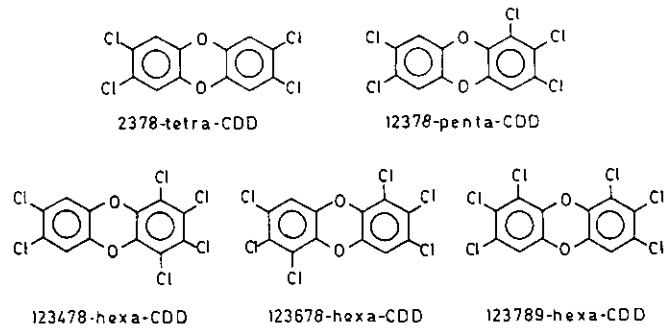

FIGURE 2. The most toxic PCDD isomers.

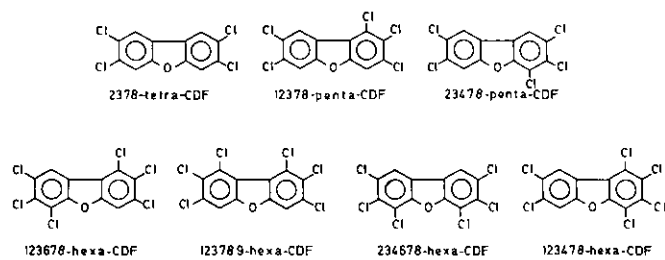

Figure 3. The most toxic PCDF isomers.

Table 3. Gas chromatography conditions used in the study.

	SE 54	SP 2330
Column length, m	25	60
Column diameter, mm	0.34	0.26
Pressure (helium), psi	21	40
Injector temperature, °C	230	230
Temperature program	100°C–2 min	100°C–2 min
	100–200°C, 20°/min	100–180°C, 20°/min
	200–300°C, 4°/min	180–260°C, 3°/min
	300°C–10 min	260°C–30 min

Table 4. Mass spectrometry conditions used in the study.

	EI	NCI
Electron energy, eV	70	120
Emission current, mA	34	34
Electron multiplyer, kV	1.5	1.5
Sensitivity, A/V	10^{-8}	10^{-8}
High vacuum, torr	5×10^{-7}	5×10^{-5}
Forepressure ionizer, torr	0.01	1.00
Ionizer temperature, °C	130	110
Manifold temperature, °C	130	130
Transmitter line temperature, °C	270	270
Interface line temperature, °C	250	250
Reagent gas	—	CH_4

Isomer-Specific HRGC/MS Analyses

We used a 25 m SE 54 capillary column for screening and a 60 m SP 2330 for the isomer specific analyses. The GC conditions are given in Table 3. A Finnigan updated

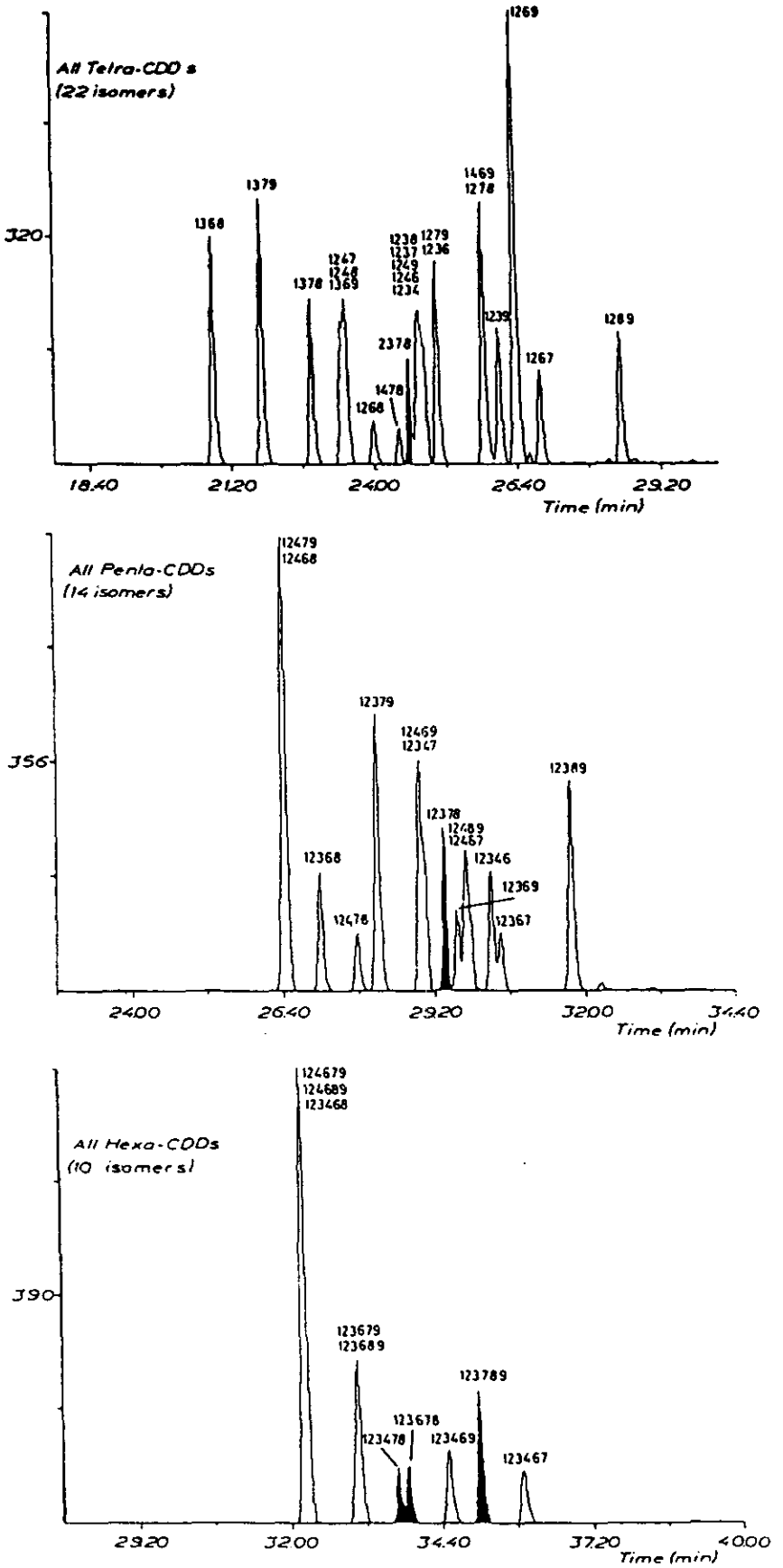

FIGURE 4. Separation of the 22 tetra-, 14 penta- and 10 hexa-CDDs on a 60 m SP 2330 column.

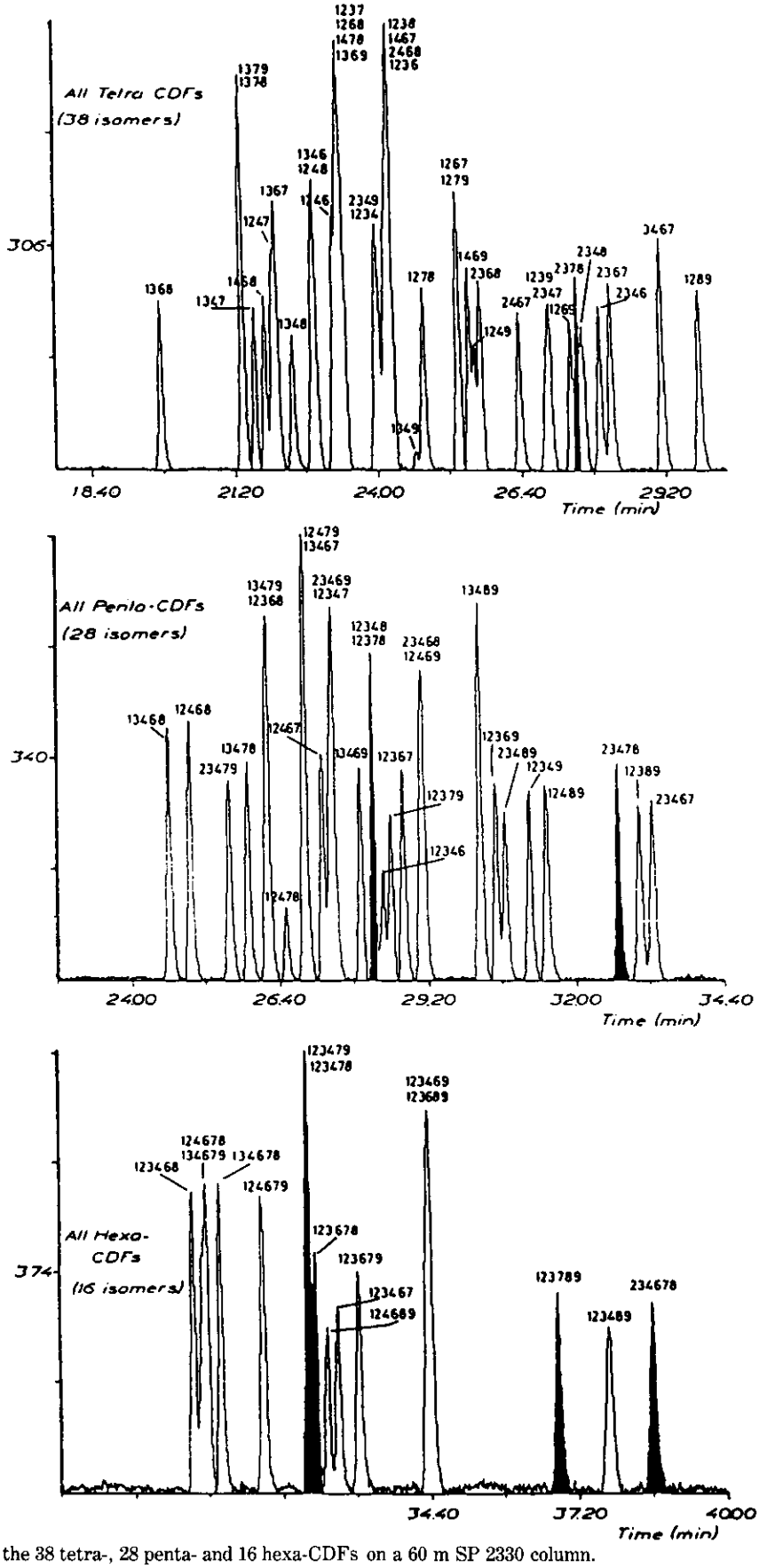

FIGURE 5. Separation of the 38 tetra-, 28 penta- and 16 hexa-CDFs on a 60 m SP 2330 column.

model 4500 MS instrument was used operating in the EI or NCI (CH_4) mode (Table 4). The capillary column was attached directly into the ion source of the MS instrument.

In our laboratory we have access to all tetra-, penta-, hexa-, hepta- and octa- isomers in the PCDD and PCDF series. The synthesis of these standards has been described elsewhere (*2–4*). The separation of these isomers using the SP 2330 column is illustrated in Figure 4 for the PCDDs and Figure 5 for the PCDFs.

The toxic 2,3,7,8-substituted isomers can be separated from the less toxic congeners; however, for the separation of the coeluting 1,2,3,7,8- and 1,2,3,4,8- as well as 1,2,3',7,8- and 1,2,3,4,6,8-isomers, a less polar column like OV 17 should be used.

Results

Transformer Fire, Binghamton, NY, USA

On February 5, 1981, a fire in the State Office Building in Binghamton, NY, USA caused a transformer to rupture, releasing soot into the whole building. The external energy source was the electricity, apparently more than 30 min elapsed until the electrical currect to the transformer was switched off. The dielectric fluid in the transformer consisted of a mixture of PCBs (65%) and chlorinated benzenes (35%).

A soot sample was analyzed and found to be highly contaminated by PCDFs and PCDDs. The total level of PCDFs was 2160 μg/g, and 20 μg/g of PCDDs were also reported (*5*). The detailed isomer-specific analysis of this soot sample is shown in Figure 6 (PCDFs) and Figure 7 (PCDDs). In this soot sample we also reported on polychlorinated biphenylenes (PCBPs) and pyrenes (PCPYs) (*5*).

The fragmentogram of the tetra-CDFs is shown in Figure 6 (upper curve). The two dominating peaks are attributed to the highly toxic 2,3,7,8- and 2,3,6,7- isomers. It was recently found that the 2,3,6,7-tetra- CDF had approximately the same AHH-induction as the 2,3,7,8-isomer (*6*). The middle curve (Fig. 6) shows the penta-CDFs and the lower curve the hexa-CDFs. The toxic 2,3,7,8-substituted isomers dominate within each group. The situation is similar in the dioxin series; the toxic 2,3,7,8-substituted isomers are quite abundant within each series (Fig. 7).

Capacitor Explosion, Stockholm, Sweden

On August 25, 1981, an explosion took place in a capacitor bank (11 kV) in an electrical power station at Danviken, Stockhom, Sweden. The exposion was caused by an electrical failure in the capacitor bank and was so violent that it caused the wall to rupture. The explosion was also associated with external arcing.

In a wipe sample collected about 1 m from the exploded capacitor, we have earlier reported that the major products were a series of chlorinated biphenylenes (PCBPs); the total levels of PCBPs was reported to be in the range of 25,000 to 30,000 ng/m^2. The existence of PCBPs was confirmed using the modern MS/MS technique. In addition to PCBPs and PCDFs we also found a series of polychlorinated pyrenes (PCPYs) (*5*). The levels of PCDFs are reported in Table 5, and the mass frangmentograms of the tetra-, penta- and hexa- CDFs are shown in the upper curves of Figures 8, 9 and 10.

Capacitor Fire, Skövde, Sweden

On March 19, 1982, a violent fire broke out in a capacitor bank (400 V) serving a high-frequency oven in a casting line of a metal treatment factory (Volvo) in Skovde, Sweden. The dielectric fluid in the capacitors consisted of mineral oil or PCB, and the two types of capacitors were mixed at random. The fire started in a capacitor containing mineral oil and spread to others also filled with mineral oil. The PCB-filled capacitors were strongly heated. A time period of 2 hr elapsed until the fire was completely extinguished. The capacitor room situated in the basement of the foundry building was burned out. Inspection revealed that the copper bars for electricity in the ceiling was partly melted (mp, 1080°C). The smoke spread in the building in an area of 60 ×30 m, and the building was efficiently ventilated through the whole time period.

The capacitor bank consisted of 40 units and 21 of these were filled with PCB, 5 kg each. An inspection after the fire showed that 12 of these capacitors were open and 9 of them were still sealed.

Four wipes were collected at the following places: on the floor in the capacitor bank; on the floor in the capacitor room close to the bank; on the wall in the capacitor room, 2 m from the bank 3 m above the floor; on a bench in the ground floor, 10 m from the oven. The quantitative results are collected in Table 5. These data show that high levels of PCDFs (> 100 ng/m^2) could only be found in an area close to the fire. At a distance of 10 m from the fire the levels were found to be about 100 times lower. The low value found in sample number 3 can be explained by the high temperature at this sampling location (the copper bars were partly melted here). The mass fragmentogram of the tetra-CDFs is given in Figure 11. The 2,3,7,8- and 2,3,6,7- isomers are major peaks eluting at the end of the chromatogram.

The major products in these samples are the polychlorinated pyrenes (Fig. 12). The di-CPYs are the dominating compounds. However, final proof cannot be obtained due to lack of synthetic standards.

Capacitor Fire, Surahammar, Sweden

On September 23, 1982, an oven at the Surahammar steel mill was ruptured by an explosion. The molten steel, 5 tons, 1500°C, ran down into the basement, passed through two safety doors (steel) and ignited a bank of capacitors consisting of 500 units filled with PCB (approx. 250 units) and mineral oil. A violent fire took place, and the whole building (140 m × 70 m × 25 m) was filled by smoke.

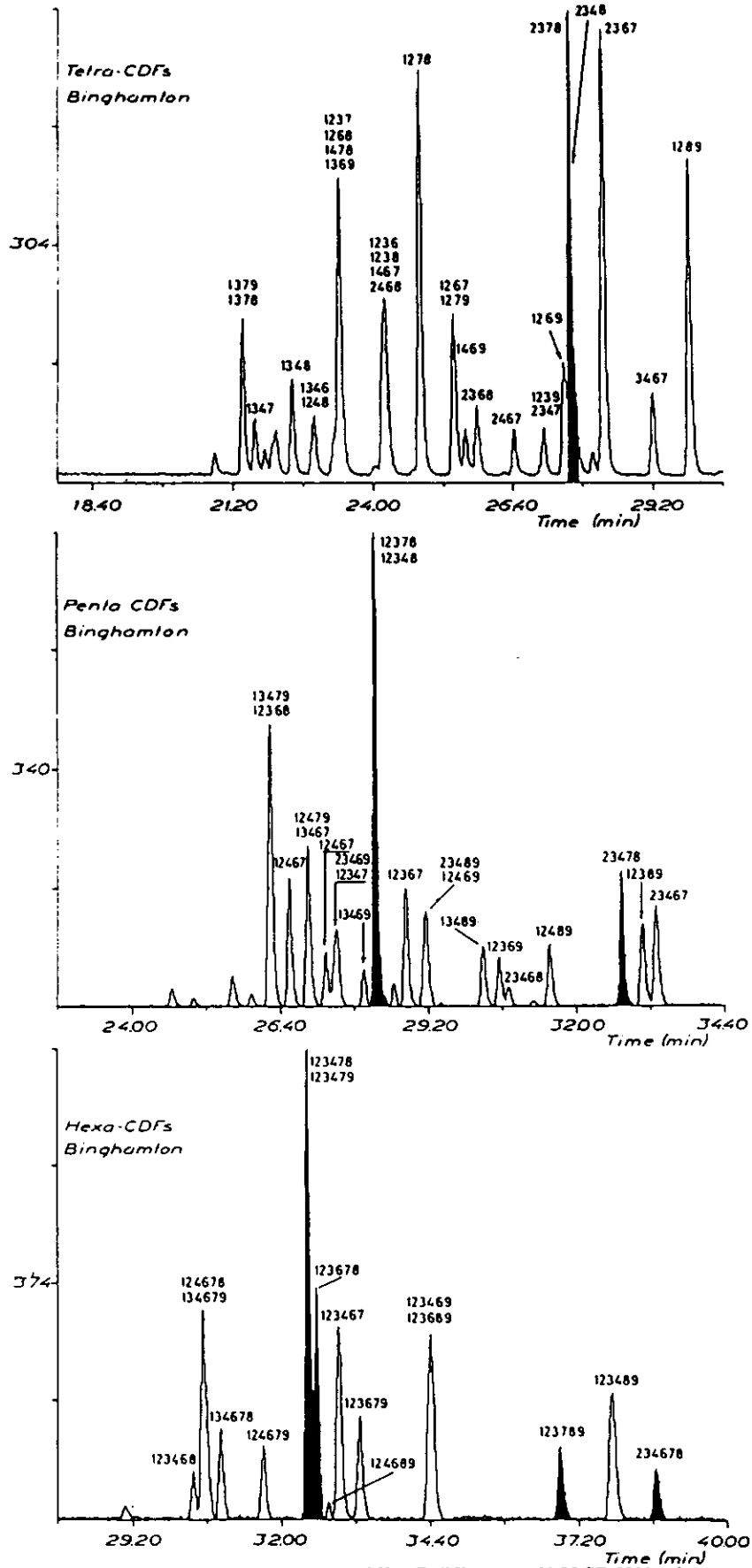

FIGURE 6. Separation of the PCDFs from the Binghamton State Office Building on a 60 M SP 2330 column.

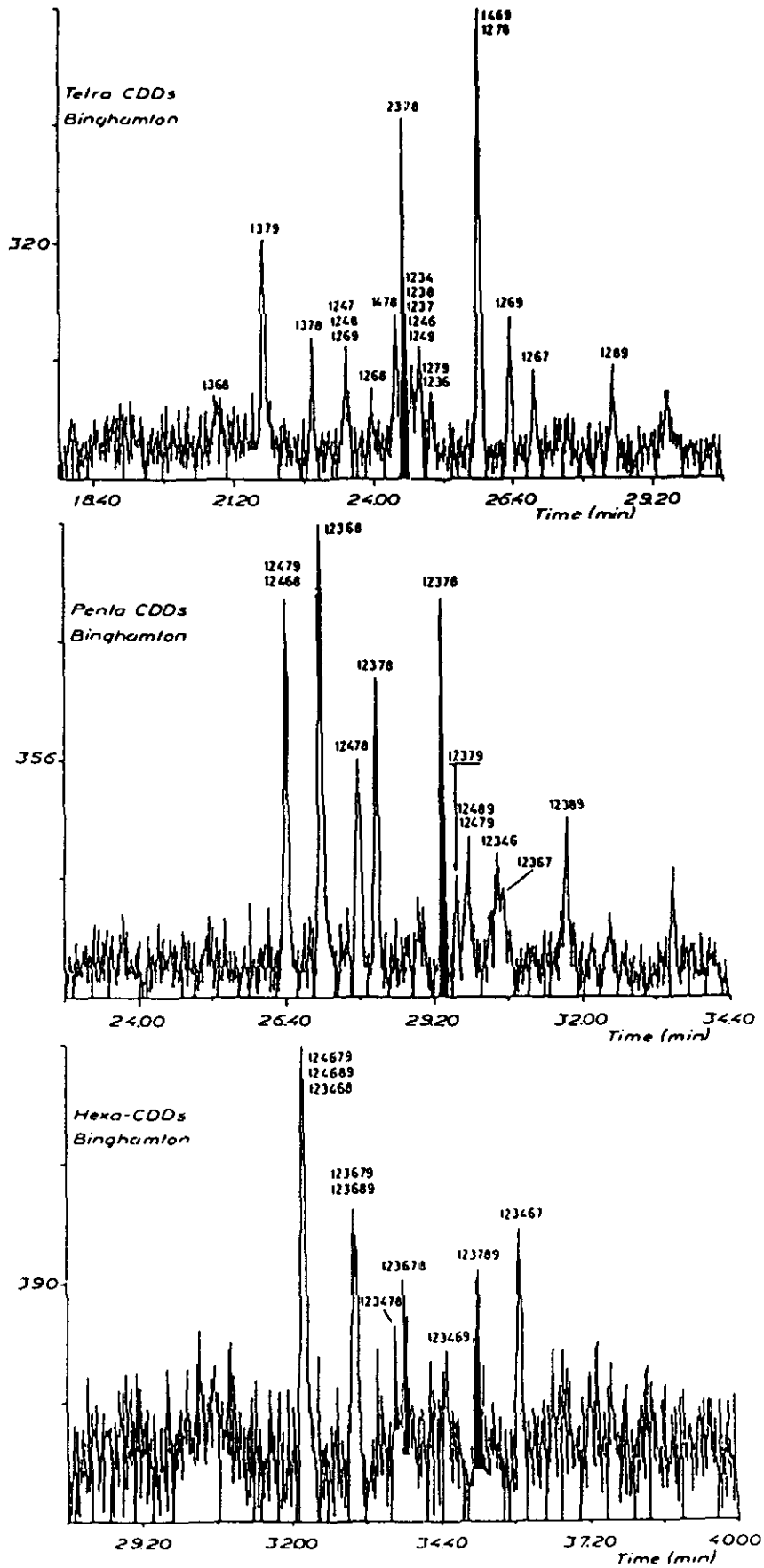

FIGURE 7. Separation of PCDDs from the Binghamton State Office Building on a 60 m SP 2330 column.

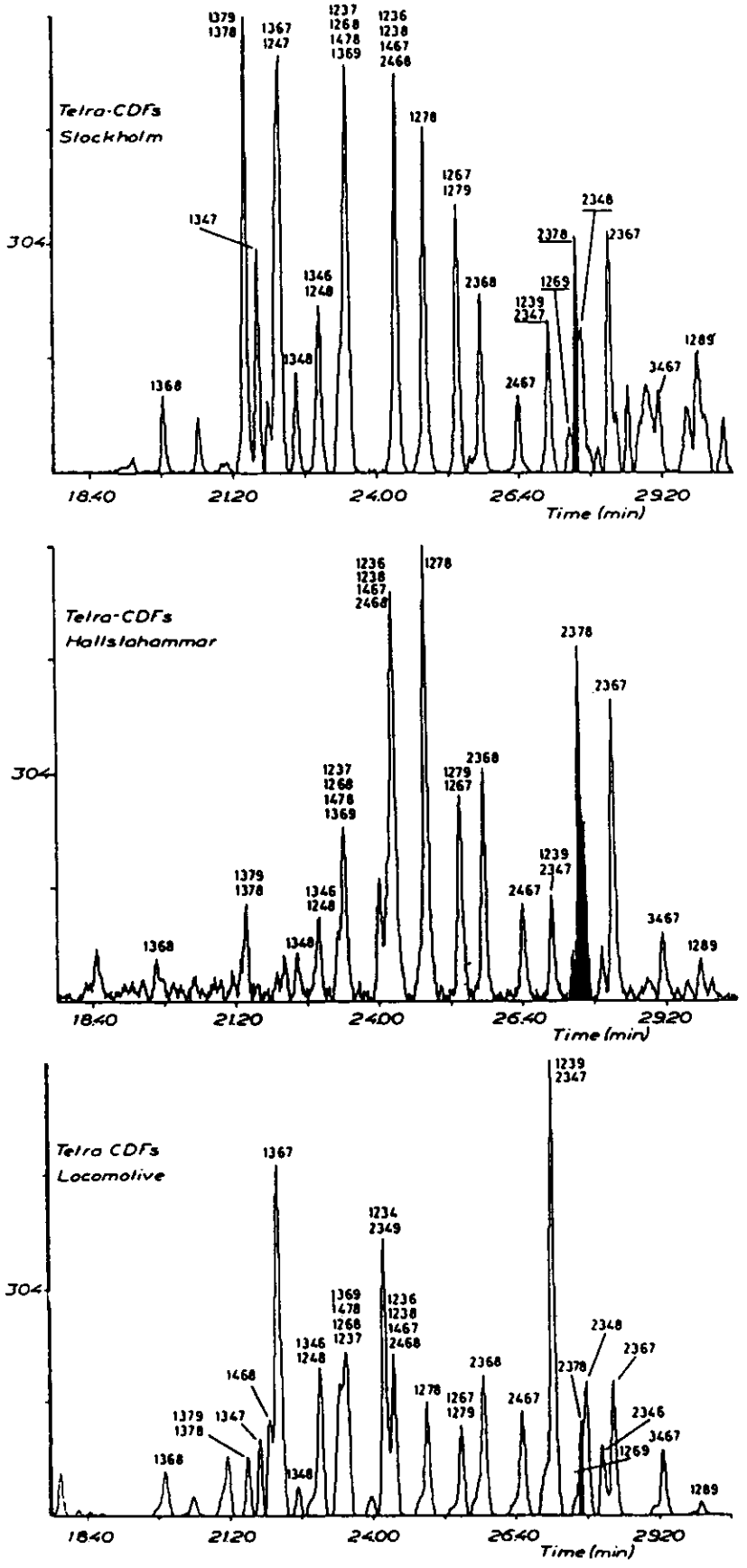

FIGURE 8. Separation of the tetra-CDFs from Stockholm, Hallstahammar and locomotive on a 60 m SP 2330 column.

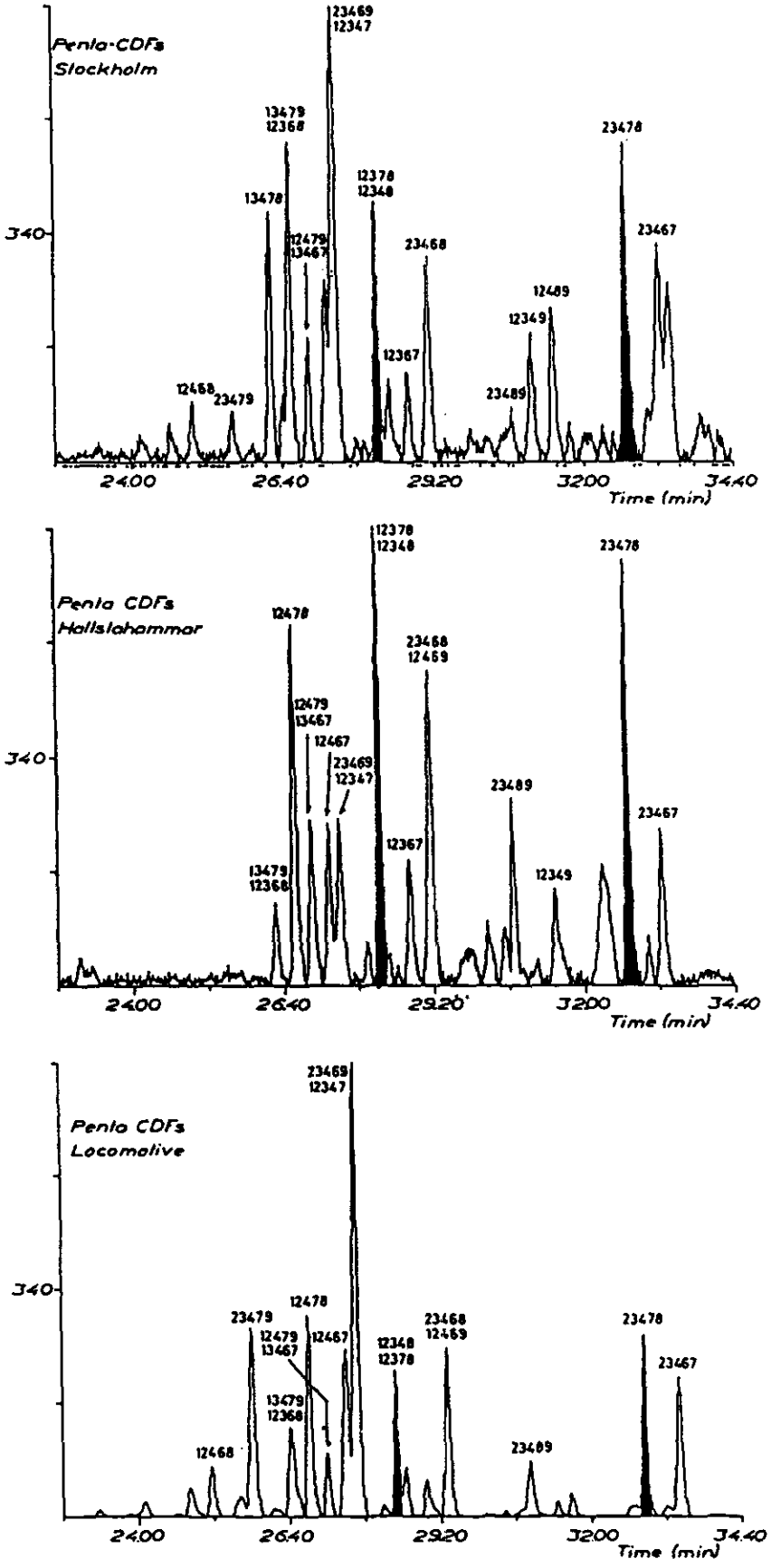

FIGURE 9. Separation of the penta-CDFs from Stockholm, Hallstahammar and railway locomotive on a 60 m SP 2330 column.

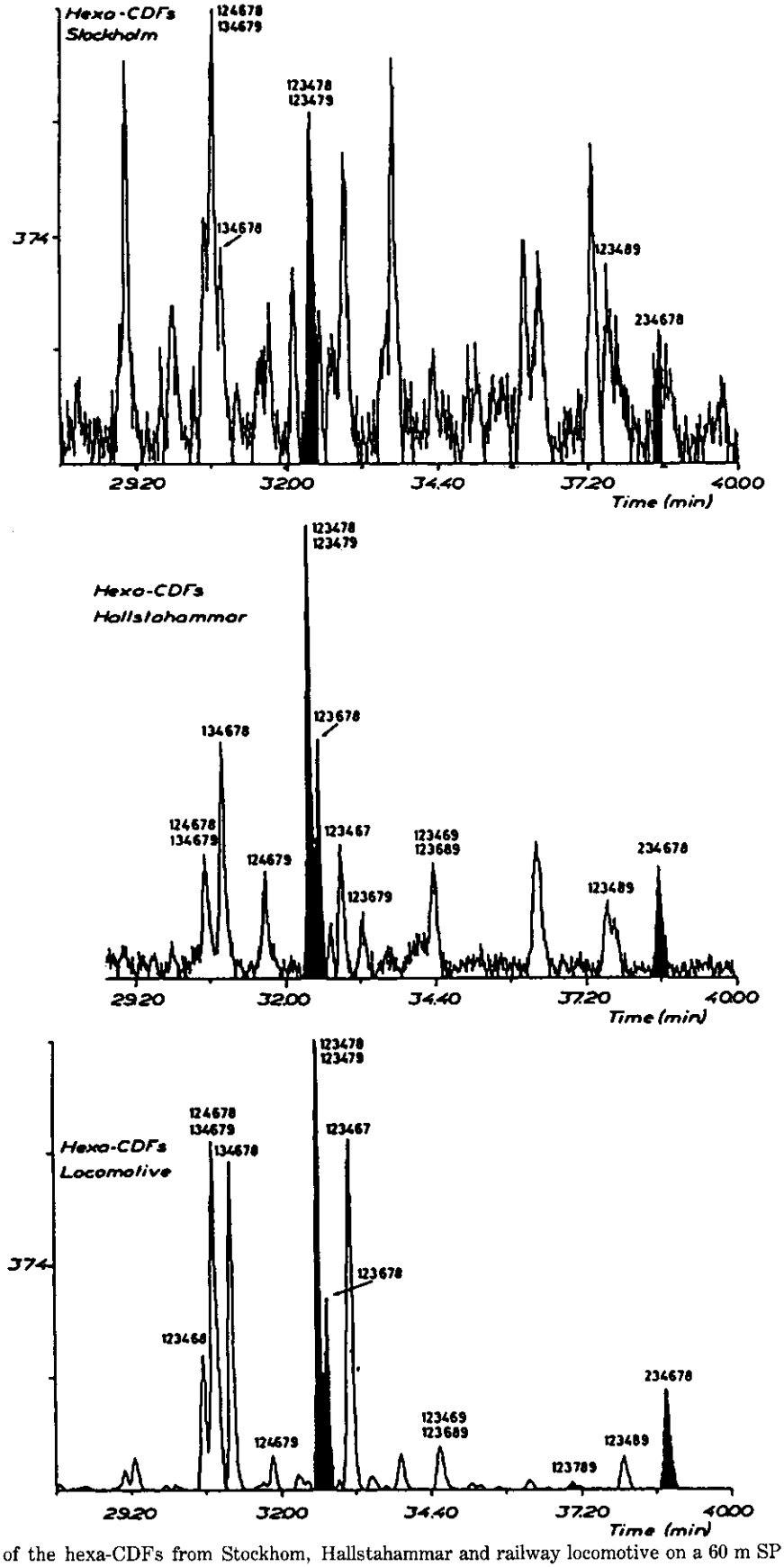

FIGURE 10. Separation of the hexa-CDFs from Stockhom, Hallstahammar and railway locomotive on a 60 m SP 2330 column.

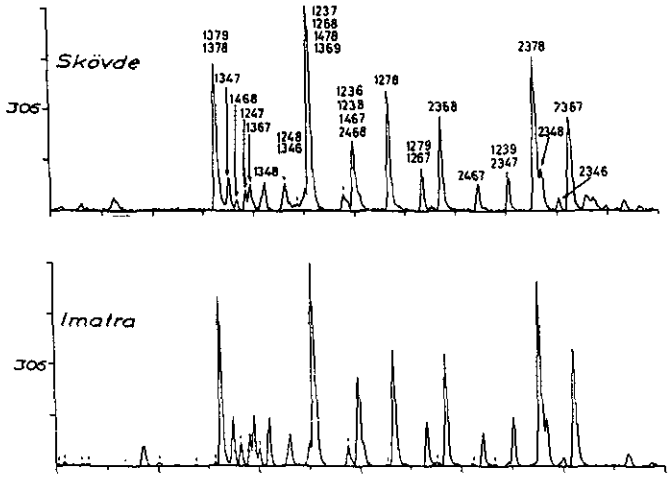

FIGURE 11. Tetra-CDFs from accidents in Skovde and Imatra separated on a 60 m SP 2330 column.

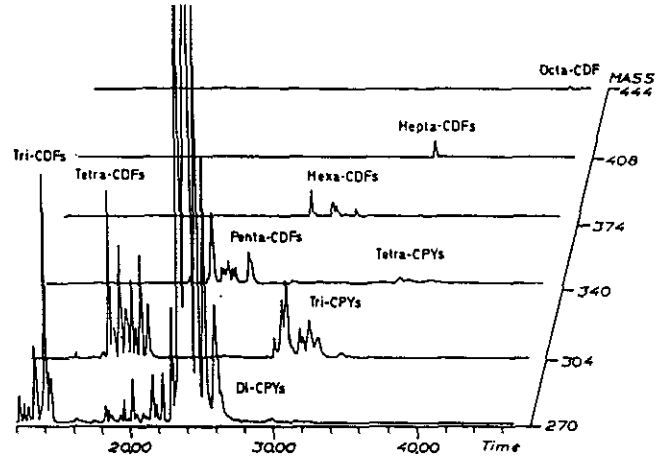

FIGURE 12. PCDFs and PCPYs from Skovde fire separated on a 25 m DB-5 column.

Immediately after the fire wipe samples were collected and analyzed (Table 6). The highest levels were found in the capacitor room and in the higher parts of the building. On the floor the levels were found to be much lower.

The building was cleaned by vacuum cleaning and high pressure washing. Due to dusting problems the washing had to be repeated. The whole operation took 3 months. Samples collected after the cleaning were analyzed in the same way and they showed a dramatic decrease in the PCDF levels (Table 6). The distribution of the individual tetra-, penta- and hexa-CDF isomers is illustrated by the fragmentograms in Figure 13.

Imatra, Finland

Early in the morning August 2, 1982, a bank of capacitors in a paper mill outside Imatra in SE Finland was destroyed by explosions and fire. A wipe test was analyzed; the levels are given in Table 5, and the fragmentogram of the tetra-CDFs in Figure 11 (lower curve). It is clear that the isomeric pattern in this sample is very similar to that found in samples from the Skövde fire.

Table 5. Levels of PCDFs (ng/m^2 or μg/g) in wipes or soot samples from Stockholm, Skövde and Imatra.

Sample	Σ Cl_4	2,3,7,8-PCDF	Σ Cl_5	Σ Cl_6	Σ Cl_7	Cl_8
Stockholm (wipe), ng/m^2	1200	100	175	0.5	<1	<1
Skövde (wipe), ng/m^2						
1	100	20	40	40	8	5
2	600	100	100	60	8	5
3	<1	<1	<1	<1	<1	<1
4	10	<1	<1	<1	<1	<1
Imatra (soot), μg/g						
1	1.0	0.07	0.2	0.04	0.02	0.01
2	16	1.0	1.0	0.3	0.2	0.1

Table 6. Levels of PCDFs (ng/m^2) in wipes from Surahammar before and after cleaning.

	Concentration, ng/m^2					
Sample	Σ Cl_4	2,3,7,8-PCDF	Σ Cl_5	Σ Cl_6	Σ Cl_7	Cl_8
Capacitor room	4000	875	3300	1800	1500	300
NE Corner, 10 m height	1250	300	355	150	65	13
NE Corner after cleaning	<20	<2	<10	<5	<10	<6
NE Corner floor	100	25	27	15	5	2
SE Corner, 10 m height	480	120	210	140	60	30
SE Corner, after cleaning	<20	<2	<20	<5	<10	<5
SE Corner floor	90	22	25	17	17	4
Outside building, 10 m downwind (ng/g)	<250	<25	<25	<60	58[a]	17[a]

[a]Possibly due to earlier use of decachlorophenyl as additive in casting wax.

Hallstahammar, Sweden

On November 8, 1982 a capacitor exploded in a foundry in Bulten-Kanthal in Hallstahammar, Sweden. The capacitor (Fig. 14) was placed close to a melting oven in the ground floor, and the fumes spread in the whole building (40 m × 15 m × 5 m). Wipe tests were collected before and after the cleaning operations; vacuum cleaning and high pressure washing. The cleaning operations were completed in one week. The quantitative results are collected in Table 7, and the fragmentograms are given in the middle curves in Figures 8–10.

Railway Locomotive, Sweden

During the fall–winter period 1982/83 another capacitor exploded in a railway locomotive in S Sweden. The accident was not reported immediately and the samples were collected in February 1983. The results are given in Table 8 and the PCDF fragmentograms are given in the lower curves in Figures 8–10.

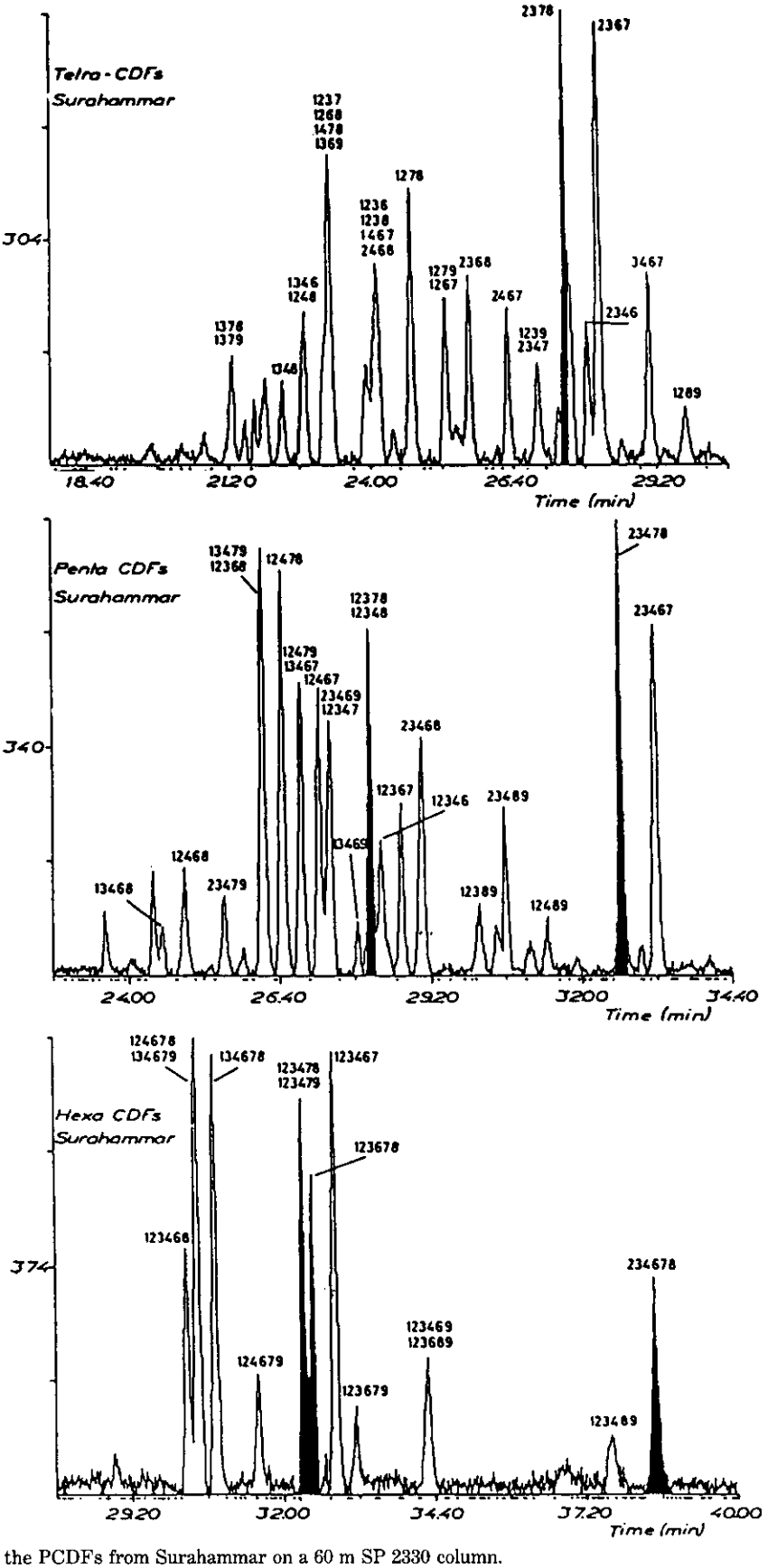

FIGURE 13. Separation of the PCDFs from Surahammar on a 60 m SP 2330 column.

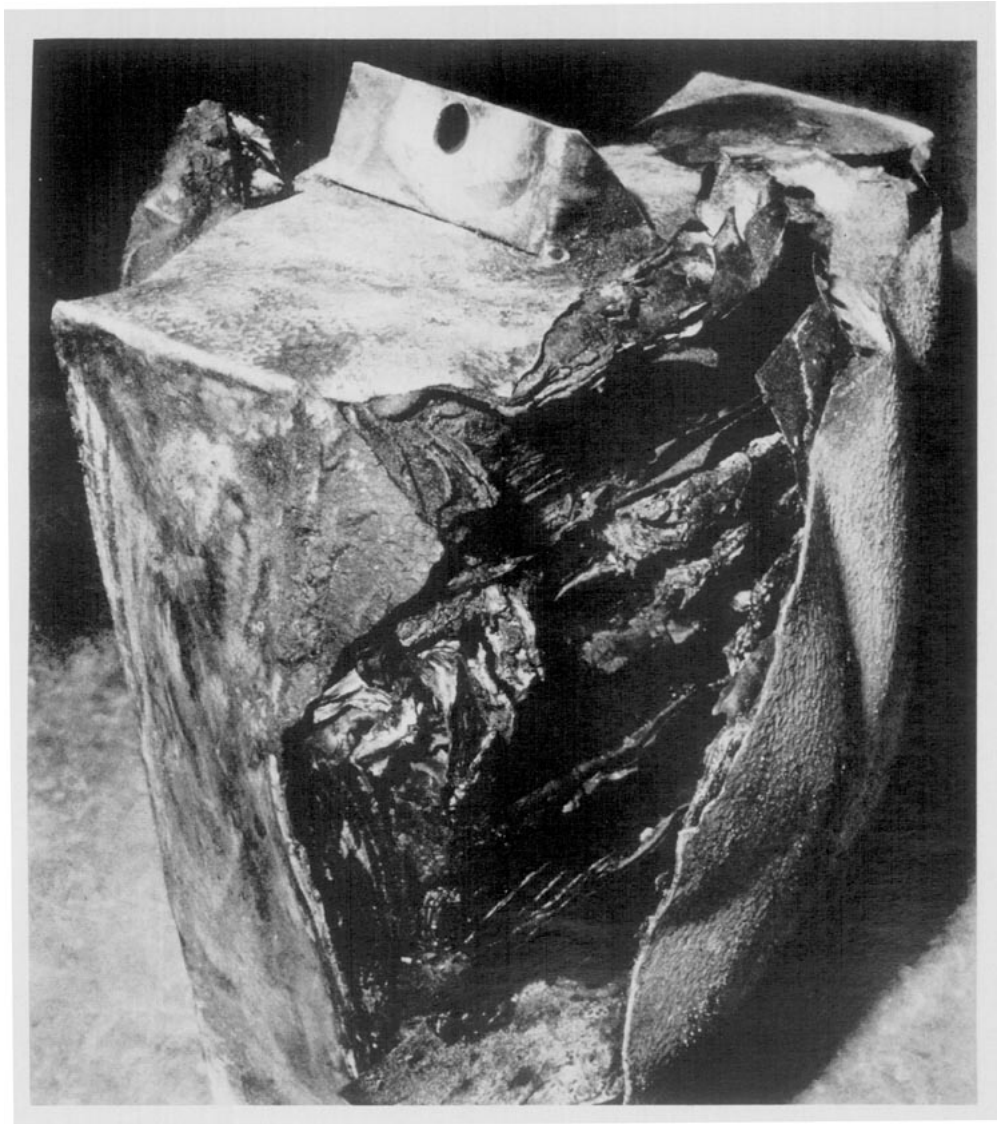

FIGURE 14. Exploded capacitor, Hallstahammar.

Table 7. Levels of PCDFs (ng/m²) in wipes from Hallstahammar before and after cleaning.

Sample	Concentration, ng/m²					
	Σ Cl_4	2,3,7,8-PCDF	Σ Cl_5	Σ Cl_6	Σ Cl_7	Cl_8
Copper bar, 2 dm above	1600	540	360	600	800	1340
Copper bar after cleaning	2	0.2	0.5	0.3	0.7	1.1
Bar, 5 m above	5000	1000	1800	850	550	440
Bar after cleaning	1	0.1	0.5	<0.1	<0.5	0.3
Floor	50	10	12	10	30	20
Floor after cleaning	<1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 8. Levels of PCDFs (ng/m²) in railway locomotive before and after cleaning.

Sample	Concentration, ng/m²					
	Σ Cl_4	2,3,7,8-PCDF	Σ Cl_5	Σ Cl_6	Σ Cl_7	Cl_8
On the floor below capacitor	69,000	1,700	29,000	14,000	6,200	1,400
On the floor after cleaning[a]	3,800	40	2,920	1,540	1,500	—
1 m from capacitor	4,900	120	1,500	400	170	40
1 m from capacitor after cleaning	90	10	73	22	12	—

[a]The paint was removed and the floor repainted.

Capacitor Explosion, Kisa, Sweden

On April 25, 1983 a PCB-filled capacitor exploded at the debarking line in a saw-mill in Kisa, Sweden. The explosion was associated with external arcing and fuming and the dielectric fluid splashed around. Three days later samples were taken and analyzed (Table 9).

Used Capacitors

We have opened some used and swollen capacitors, collected and analyzed the drained PCB. The levels of PCDFs was approximately 2 ppm, mainly tetra-CDFs, which is similar to the levels we found for the new and unused PCB (Prodelec 30 10). Examination of the paper

Table 9. Levels of PCDFs (ng/m²) in wipes from Kisa saw mill before and after cleaning.

Sample	Concentration, ng/m²					
	Σ Cl_4	2,3,7,8-PCDF	Σ Cl_5	Σ Cl_6	Σ Cl_7	Cl_8
Near exploded capacitor	100,000	40,000	NA[a]	NA	NA	NA
Near exploded capacitor after cleaning	<90	<21	70	30	<10	5
Closed operator room	500	125	NA	NA	NA	NA
Closed operator room after cleaning	<12	<5	<5	<5	<5	5

[a] NA = not analyzed.

layer revealed dark spots, probably caused by electrical arcing. The PCB around these dark spots was extracted and analyzed. The levels were similar to the levels found in the drained PCB or new PCB.

Sparking Experiments in PCB

No increase in PCDFs (ca. 2 ppm) could be found after up to 7 sparks (18 kV, 2 μF) in pure PCB. No PCBPs could be found; the ratio PCDFs:PCBPs was greater than 100:1. In another experiment 1% of 1-epoxyethyl-3,4-epoxycyclohexane (Union Carbide ERL 42 06) was added before the sparking (4 sparks, 15 kV, 2.5 μF). In this experiment, the PCDF levels increased (Fig. 15). In general the level of PCDFs increased ten times, but for a few isomers the increase was 30-fold; for others no increase was found. The ratio PCDFs:PCBPs was greater than 100:1.

Conclusions

All the PCB fires and capacitor explosions studied have resulted in formation of toxic polychlorinated dibenzofurans. In some cases, which all seem to be associated with external arcing, we have also found PCBPs. Only in samples from the Binghamton State Office Building were PCDDs including 2,3,7,8-tetra- CDD found. Possible precursors to the dioxins are chlorinated benzenes.

The pattern of PCDF isomers was studied by using a SP 2330 column. The same isomers were found in all samples, but some variation was found, especially for the toxic 2,3,7,8-tetra-CDF. This isomer was a major constituent in the samples from Binghamton and Surahammar, but a middle (minor) constituent in the samples from some of the capacitor explosions. After cleaning the levels were dramatically reduced. Vacuum cleaning and high pressure washing was used to clean contaminated areas.

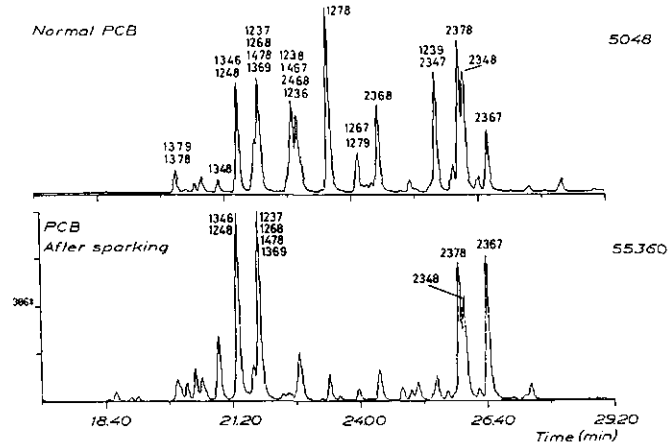

FIGURE 15. Separation of tetra-CDFs from normal PCBs and PCBs after sparking on a SP 2330 column.

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